

**THERMOBARIC EXPLOSIVE****STATEMENT REGARDING FEDERALLY SPONSORED  
RESEARCH OR DEVELOPMENT**

5       The invention described herein may be manufactured and used by or for the government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

**BACKGROUND OF THE INVENTION**

10    Field of the Invention

      The invention disclosed herein relates to explosive formulations with improved combustion efficiency. More particularly, the explosive formulations of the invention are capable of maintaining a relatively high blast pressure in an oxygen poor environment, such as a tunnel or other confined spaces.

15    Description of the Related Art

      There is a long history of studying blast explosives, reactive metals and associated metal combustion technologies. The success of the development of Solid Fuel-Air-Explosive (SFAE) has been demonstrated providing 30-40% increased internal blast over a conventional explosive. SFAE is a singular event with combined mixing and initiation of the reaction. In confined spaces,  
20   transition to full detonation is not required for enhanced blast, if the solid fuel is ignited early in

the dispersion process. A series of reflective shock waves generated by the detonation mixes the hot detonation gases with metal particles and compresses the metal particles at the same time.

These actions provide the chemical kinetic support to maintain a hot environment, causing more metal to ignite and burn. This late time metal combustion process produces a significant pressure

5 rise over a longer time duration (10-50 msec). This is a phase generally referred to as after burning or late-time impulse which can occur outside of where the detonation occurred, resulting in more widespread damage.

Aluminum has been used as the metal of choice, due to high heat of combustion, cost and availability. Billets of SFAE made with Al, provide savings in volume with increased fuel mass

10 for blast performance. However, combustion efficiency has been an issue, especially in the event that the fuel content (35-60 wt%) is high with respect to the total weight of explosive composition. Poor combustion efficiency is often observed in many of the thermobaric warhead tests, which causes the severe ineffectiveness of the weapon. This is due to the high ignition temperature, 2200 K, typically required for proper combustion of AL. During the burning of Al,

15 heat is produced and aluminum oxide is formed. However, the burning of all the metal to completion requires maintaining the hot environment. This environment can be best maintained if it is supported chemically by the combustion of other oxidizer species (i.e. AP or nitrate ester liquid, IPN (isopropyl nitrate)) that are much easier to ignite (AP has an ignition temperature of 250 C and IPN has a low flash point of 22 C). The combustion of these additives produce the hot

20 gases to support the burning of metal, thus 100% combustion efficiency can be obtained. Metal

composites, metal and oxidizer combined granules, produced from coating of particles with a binder, can be made easily with techniques well known in the art.

Another combined approach to further improve the metal combustion efficiency is to use a more reactive metal as part of or as the entire metal fuel component. New reactive metal materials such as nano-sized aluminum to increase the reactivity, titanium and boron alloy to increase the thermal output, and magnesium/aluminum alloy to lower the ignition temperature are among the most promising approaches to increase the metal combustion efficiency. More powerful explosives such as CL-20 that are capable of raising the detonation pressure and temperature are also extremely beneficial.

There exists a need in the art for new explosive formulations with new reactive metal and metal composites to have 50-100 % higher blast energy than those by the baseline composition such as Tritonal or PBX N109. Further, the new formulations coupled with new warhead designs will have the potential to form one of the most powerful thermobaric warheads, when compared to the weapon systems that currently exist.

### **SUMMARY OF THE INVENTION**

A preferred embodiment of the present invention is a metal composite that combines a binder, a reactive metal and an oxidizer. In a more preferred embodiment of the present invention, a plasticizer and a catalyst may be added. In another preferred embodiment of the present invention, the binder is selected from those polymers capable of coating the reactive

metal and oxidizer powder. Two of the preferred methods to produce the compositions of the current invention are:

- (1) The coated powder forms the fuel charge through pressing, combining this fuel charge with a high explosive charge (HMX, RDX or CL-20 based PBX's) in an annular design to make up the fill for the warhead.
- (2) Using metal or metal/oxidizer powders in a mixing, casting and curing process to combine with high explosive to form castable PBX's. The reactive metal contains ingredients that are intrinsically reactive with the reaction products of high explosive and oxidizer with or without the presence of high concentration of oxygen.

A preferred embodiment of the present invention discloses a metal composite comprising about 60.0 to about 96.0 weight % of at least one reactive metal, about 4.0 to about 10.0 weight % of at least one binder and about 0.0 to about 36.0 weight % of an oxidizer. The reactive metal may be selected from the group consisting of nano-sized metal particles, metastable mechanical alloy and any combination thereof. More specifically, the reactive metal may be selected from the group consisting of nano-sized aluminum, nano-sized boron and nano-sized titanium, nano-sized magnesium, Al-Mg, Al-Mg-H, B-Mg, Al-B and Ti-B. The binder may be selected from the group consisting of copolymer of vinylidene fluoride hexafluoropropylene, nitrocellulose, GAP and Zeon.

A preferred embodiment of the present invention relating to castable compositions discloses an explosive having an annular design. The explosive comprises a cylindrical shell of

solid fuel air explosive surrounding a cylindrically shaped high explosive. The solid fuel air explosive may be selected from the group consisting of reactive metal and metal composite. The metal composite comprises about 60.0 to about 80.0 weight % of at least one reactive metal, about 4.0 to about 8.0 weight % of at least one binder and about 0.0 to about 36.0 weight % of an oxidizer. The reactive metal may be selected from the group consisting of nano-sized metal particles, metastable mechanical alloy and any combination thereof. More specifically, the reactive metal may be selected from the group consisting of nano-sized aluminum, nano-sized boron and nano-sized titanium, nano-sized magnesium, Al-Mg, Al-Mg-H, B-Mg, Al-B and Ti-B, H-2 (2  $\mu$ m spherical aluminum) and H-5 (5  $\mu$ m spherical aluminum). The oxidizer may be selected from the group consisting of ammonium perchlorate, ammonium dinitramide and ammonium nitrate.

One object of a preferred embodiment the present invention is to provide an explosive with enhanced combustion efficiently capable of sustaining a high pressure over a period of time in a confined environment with a limited oxygen supply.

Another object of a preferred embodiment the present invention is to provide an explosive capable of maintaining a relatively high pressure (30- 60 psi) for up to 50 msec in an environment characterized with high rate of thermal quenching (cold air), this environment has a profound adverse effect for metal combustion, which is the main cause for combustion efficiency.

Another object of a preferred embodiment the present invention is to provide an

Another object of a preferred embodiment the present invention is to provide thermobaric explosive formulations with reactive metals and metal composites which have a 100% higher blast energy than compositions such as Tritonal and PBX N109.

5           These and other objects of the invention will become more clear when one reads the following specification, taken together with the drawings that are attached hereto. The scope of protection sought by the inventors may be gleaned from a fair reading of the Claims that conclude this specification.

### BRIEF DESCRIPTION OF THE DRAWINGS

**Figure 1 is a sectional view of a typical explosive having an annular design.**

## DETAILED DESCRIPTION OF THE INVENTION

15 efficiently capable of sustaining a high pressure over a period of time in a confined environment,  
such as an air tight room or a cave, where oxygen may be in limited supply.

20 aluminum, such as Alex®, boron, manganese and titanium, those having a size of about 20-500

nm. The metastable mechanical alloys include Al-Mg, Al-Mg-H, B-Mg, Al-B, Ti-B, H-2 and H-5 made from high energy milling. The metastable mechanical alloys are nano-crystalline metastable phases with particle sizes of about 1-50  $\mu\text{m}$ . The reactive metal used may also include Ti, B or Mg. In a preferred embodiment of the present invention, the reactive metal  
5 comprises about 60.0-80.0 weight % of the total metal composite, preferably at about 74.0 weight %.

The thermobaric explosive formulations of a preferred embodiment of the present invention incorporate high energy explosive material such as hexa-nitro-hexa-aza-isowurtzitane (CL-20), cyclotrimethylenetrinitramine (RDX) and cyclotetramethylene tetranitramine (HMX).  
10 The powerful oxidizers, such as ammonium perchlorate (AP), ammonium dinitramide (ADN), ammonium nitrate (AN) and barium nitrate are selected to be used in the metal composite or castable PBX's. A preferred embodiment of the present invention uses ammonium perchlorate (AP) particles, preferably about 11-100  $\mu\text{m}$  in size. The oxidizer comprises about 12.0-36.0 weight % of the total metal composites, preferably at about 20.0 weight %.

15 The binder is selected from those polymers capable of coating the reactive metal and high explosive powder. Preferably the binder is selected from the group consisting of copolymer of vinylidene fluoride hexafluoropropylene, such as Viton®, nitrocellulose, glycidyl azide polymer (GAP) or an acrylic acid ester polymer, such as Zeon®. In a preferred embodiment of the present invention, the binder comprises about 4.0-6.0 weight % of the total metal composites, preferably  
20 at about 4.0 weight % for the total metal composite. The binders used for castable PBX's may be

hydroxy-terminated polybutadienes (HTPB), hydroxy-terminated polycaprolactone (PCP), hydroxy-terminated polyesters, hydroxy-terminated polyethers (HTPE), Glycidyl azide polymer (GAP), trifluoroethyl-terminated poly (1-cyano-1-difluoramino)-polyethylene glycol (PCDE) and any combination thereof. Typically, 5.0 to 7.0 weight % is used for castable PBX version.

5 In a more preferred embodiment, a plasticizer and a burn rate catalyst may be added. The preferred plasticizer is *bis*-(2,2-ro-2-fluoroethyl) formal (FEFO). However, other plasticizers may be utilized, including energetic plasticizers selected from those compounds, which are liquids and contain energetic moieties or groups in their chemical structures. These moieties can include nitro or nitrate ester groups, azido groups, or nitramino groups. Suitable plasticizers  
10 include TEGDN (triethyleneglycol dinitrate), or Butyl NENA (n-butyl-2-nitratoethyl-nitramine). Other suitable plasticizers include DEGDN (diethyleneglycol dinitrate), TMETN (trimethylolethane trinitrate), and BTTN (butanetriol trinitrate). These plasticizers may be used independently or in combination. Other fluoramino groups such as *bis*-(2,2-ro-2-fluoroethyl) formal (FEFO) and *bis*-[2, 2-*bis*(difluoramino)-5, 5-dinitro-5-fluoropentoxy] methane (SYFO)  
15 may be incorporated into the formulations. In a preferred embodiment of the present invention, the plasticizer comprises about 4.0 weight % of the formulations.

Iron oxide ( $\text{Fe}_2\text{O}_3$ ), nano-sized is a suitable burn rate catalyst and is preferable to exotic burn rate catalysts such as superfine iron oxide, chromic oxide, catocene, or carboranes.

Aluminum oxide may also be used. In a preferred embodiment of the present invention, the burn  
20 rate catalyst comprises about 1.0 weight % of the total metal composites. Tables I and II disclose



a number of the preferred formulations of the present invention.

Reactive Metal	Oxidizer	Binder	Plasticizer	Catalyst
80% H-5	14% AP, 11 $\mu\text{m}$	6% Viton <sup>®</sup>	None	None
60% H-5, 20% Al/Mg alloy, 28 $\mu\text{m}$	14% AP, 11 $\mu\text{m}$	6% Viton <sup>®</sup>	None	None
80% H-5	12% AP, 11 $\mu\text{m}$	6% Viton <sup>®</sup>	None	1% Fe <sub>2</sub> O <sub>3</sub> , nano-sized
74% H-5	20% AP, 11 $\mu\text{m}$	6% Viton <sup>®</sup>	None	1% Fe <sub>2</sub> O <sub>3</sub> , nano-sized
37% Ti, 44 $\mu\text{m}$ 37% B, 0.6-7 $\mu\text{m}$	21% AP, 11 $\mu\text{m}$	6% Nitrocellulose	None	None
74% Ti-B, 20 $\mu\text{m}$	21% AP, 11 $\mu\text{m}$	6% Nitrocellulose	None	None
74% Mg-B, 20 $\mu\text{m}$	21% AP, 11 $\mu\text{m}$	6% Nitrocellulose	None	None
50% H-5 24% Alex <sup>®</sup> 0.2 $\mu\text{m}$	20% AP, 11 $\mu\text{m}$	5% Nitrocellulose	None	1% Fe <sub>2</sub> O <sub>3</sub> , nano-sized
50% H-5 24% Alex <sup>®</sup> 0.2 $\mu\text{m}$	20% AP, 11 $\mu\text{m}$	4% Nitrocellulose	4% FEFO	1% Fe <sub>2</sub> O <sub>3</sub> , nano-sized
74% Alex <sup>®</sup> , 0.2 $\mu\text{m}$	20% AP, 11 $\mu\text{m}$	5% Nitrocellulose	None	1% Fe <sub>2</sub> O <sub>3</sub> , nano-sized
40% Flake Al, 20% Al/Mg alloy	36% AP, 100 $\mu\text{m}$	4% Viton <sup>®</sup>	None	None

Note: Al/Mg milled in batch MA020129-01, Ti-B milled in batch MA020317-01, and Mg-B milled in batch MA020319-01 at New Jersey Institute of Technology, Newark, New Jersey.

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TABLE I

Chemical Composition of Metal Composite Coated by Various Binders

Reactive Metal	Oxidizer	Binder	High Explosive	Plasticizer & Catalyst
20-40%	15-35% AP, 11-100 $\mu$ m	10-15% HTPB	30-55% HMX	4-6%
Metal Composite		Binder	High Explosive	Plasticizer
40-60%	None	10-15% HTPB	30-45% HMX or 30-50% HMX	None
40-60%	None	10-15% LMA	30-45% HMX	None
30-55%	None	10-15% HTPB	35-60% CL-20	None
20-24%	15-35% AP	10-15% HTPB	30-55% HMX	None

Note: metal composite contains oxidizer

TABLE II

#### Typical Composition of Castable PBX's Containing Reactive Metal and AP Oxidizer

5        The novel thermobaric explosives of the present invention are spherical particles of composite material containing high explosive, oxidizer, reactive metal and binder. Plasticizer and burn rate catalyst may be added to manipulate performance. A method of making the novel thermobaric explosives described herein is disclosed in US Patent No. 5,750,921 issued to Chan et al. on May 12, 1998, hereby incorporated herein by reference.

10        In a preferred embodiment of the present invention, a solid fuel-air explosive annular design is used as shown in Figure 1. In a typical annular design, a cylindrical shell of solid fuel air explosive (SFAE) 22 surrounds the high explosive 21. As a matter of preference, the shapes of the high explosive charge are preferably spherically or cylindrically symmetric, to provide a

uniform dispersion pattern. Solid metal casings 23 are typically pressed from reactive metal powder or metal composite (listed in Table 1) as SFAE. These solid metal casings are typically machined from stock into billets, but can also be manufactured by other methods such as casting or forging. The SFAE is then pressed into solid billets with a density (preferred to be 80-90%  
5 TMD) applicable to the particular use. The annular design preferably uses flake aluminum as the reactive metal. The SFAE billets are then placed in the warhead and the explosive is cast or pressed into place. The final SFAE fuel to explosive ratio is dependent upon the size and configuration of the warhead. PBX N112 consists of 89% HMX (high explosive) and 11% LMA (lauryl methacrylate). The PBX N112/reactive metal weight ratio is preferably in the range 0.66  
10 to 1.45, most preferably the ratio is 1.0.

In another preferred embodiment, the compositions of the present invention are formed into a unicharge. The unicharge design preferably uses spherical aluminum as the reactive metal. Table II discloses preferred ranges of ingredients for the formulations of the unicharge  
embodiment. As noted previously, a plasticizer and/or a burn rate catalyst may be added to the  
15 formulations to tailor the formulations to particular needs. Although specific binders are listed, any of the binders previously noted may be used in the formulations. Similarly, any of the oxidizers previously noted may be substituted for AP and any of the high explosives previously noted may be substituted for HMX.

Although the description above contains many specificities, these should not be construed  
20 as limiting the scope of the invention but as merely providing an illustration of the presently

preferred embodiment of the invention. Thus the scope of this invention should be determined by the appended claims and their legal equivalents.

**CLAIMS**

What is Claimed is:

1. A metal composite comprising:

about 60.0 to about 96.0 weight % of at least one reactive metal;

5 about 4.0 to about 10.0 weight % of at least one binder; and

about 0.0 to about 36.0 weight % of an oxidizer.

2. The metal composite composition of Claim 1, wherein said reactive metal is selected from the group consisting of nano-sized metal particles, metastable mechanical alloy and any combination

10 thereof.

3. The metal composite composition of Claim 1, wherein said reactive metal is selected from the group consisting of nano-sized aluminum, nano-sized boron and nano-sized titanium, Al-Mg, Al-Mg-H, B-Mg, Al-B, Ti-B, H-2 and H-5.

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4. The metal composite composition of Claim 2, wherein said nano-sized metal has an average particle size of about 200 nm to about 500 nm.

5. The metal composite composition of Claim 2, wherein said metastable mechanical metal alloy

20 has an average particle size of about 1 $\mu$ m to about 50 $\mu$ m.

6. The metal composite composition of Claim 1, wherein said binder is selected from the group consisting of copolymer of vinylidene fluoride hexafluoropropylene, nitrocellulose, GAP and Zeon.

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7. An explosive composition comprising:

about 20.0 to about 70.0 weight % of at least one metal composite;

about 10.0 to about 15.0 weight % of at least one binder; and

about 20.0 to about 60.0 weight % of high explosive.

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8. The explosive composition of Claim 7, wherein said metal composite comprises:

about 60-80 weight % of reactive metal; and

about 14.0 to about 36.0 weight % oxidizer.

15 9. The explosive composition of Claim 7, wherein said metal composite is about 40.0 to about 60.0 weight % and said high explosive is about 30.0 to about 50.0 weight %.

10. The explosive composition of Claim 9, wherein said binder is HTPB and said high explosive is HMX.

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11. The explosive composition of Claim 7, wherein said high explosive is selected from the group consisting of CL-20, RDX and HMX.

12. The explosive composition of Claim 8, wherein said oxidizer is selected from the group  
5 consisting of AP, ADN, AN, and barium nitrate.

13. The explosive composition of Claim 8, wherein said oxidizer is about 15.0 to about 35.0 weight %, said binder is HTPB, and said metal composite is about 20.0 to about 40.0 weight %.

10 14. The explosive composition of Claim 8, wherein said reactive metal is selected from the group consisting of nano-sized metal particles, metastable mechanical metal alloy and any combination thereof.

15 15. The explosive composition of Claim 8, wherein said reactive metal is selected from the group consisting of nano-sized aluminum, nano-sized boron and nano-sized titanium, nano-sized magnesium, Al-Mg, Al-Mg-H, B-Mg, Al-B, Ti-B, Ti, B, Mg, H-2 and H-5.

16. The explosive composition of Claim 14, wherein said nano-sized metal has an average particle size of about 200 nm to about 500 nm.

17. The explosive composition of Claim 14, wherein said metastable metal alloy has an average particle size of about 1 $\mu$ m to about 50 $\mu$ m.

18. The explosive composition of Claim 7, wherein said binder is selected from the group  
5 consisting of HTPB, PCP, hydroxy-terminated polyesters, HTPE, GAP, LMA and PCDE.

19. An explosive charge composition comprising:

about 15.0 to about 35.0 weight % of AP;

about 20.0 to about 40.0 weight % of a reactive metal;

10 about 10.0 to about 15.0 weight % of at least one binder; and

about 30.0 to about 55.0 weight % of high explosive.

20. The explosive charge composition of Claim 19, wherein said high explosive is about 30.0 to about 45.0 weight %.

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21. The explosive charge composition of Claim 19, wherein said high explosive is selected from the group consisting of CL-20, RDX and HMX.

22. The explosive charge composition of Claim 19, wherein said reactive metal is selected from  
20 the group consisting of nano-sized metal particles, metastable mechanical metal alloy and any



combination thereof.

23. The explosive charge composition of Claim 22, wherein said reactive metal is selected from the group consisting of nano-sized aluminum, nano-sized boron and nano-sized titanium, nano-  
5 sized magnesium, Al-Mg, Al-Mg-H, B-Mg, Al-B, Ti-B, Ti, B, Mg and H-2 and H-5.

24. The explosive charge composition of Claim 23, wherein said nano-sized metal has an average particle size of about 200 nm to about 500 nm.

10 25 The explosive charge composition of Claim 22, wherein said metastable metal alloy has an average particle size of about 1 $\mu$ m to about 50 $\mu$ m.

26. The explosive charge composition of Claim 19, wherein said binder is selected from the group consisting of HTPB, PCP, hydroxy-terminated polyesters, HTPE, GAP, LMA and PCDE.

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27. The explosive charge composition of Claim 19, wherein said binder is LMA.

28. The explosive charge composition of Claim 19, wherein said binder is LMA, said high explosive is HMX, and said metal composite is about 40.0 to 60.0 weight %.

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**29. A solid fuel air explosive, comprising:**

**a first grain, wherein said first grain is a high explosive;**

**a second grain, wherein said second grain is a metal fuel grain;**

**about 4.0 to about 6.0 weight % of at least one binder; and**

**5        about 14.0 to about 36.0 weight % AP.**

**30. The solid fuel air explosive of Claim 29, wherein the ratio of said second grain to said first grain is about .66 to about 1.45.**

**10    31. The solid fuel air explosive of Claim 29, wherein the ratio of said second grain to said first grain is about 1.0.**

**32. The solid fuel air explosive of Claim 29, wherein the said first grain comprises:**

**about 87-90 weight % HMX; and**

**15    about 10-13 weight % binder, wherein said binder is selected from the group consisting of  
HTPB, PCP, hydroxy-terminated polyesters, HTPE, GAP, LMA and PCDE.**

**33. The solid fuel air explosive of Claim 29, wherein said metal fuel grain is selected from the group consisting of reactive metal and metal composite.**

34. The solid fuel air explosive of Claim 33, wherein said reactive metal is selected from the group consisting of nano-sized metal particles, metastable mechanical alloy and any combination thereof.

5 35. The solid fuel air explosive composition of Claim 33, wherein said reactive metal is selected from the group consisting of nano-sized aluminum, nano-sized boron and nano-sized titanium, nano-sized magnesium, Al-Mg, Al-Mg-H, B-Mg, Al-B, Ti-B, Ti, B, Mg and H-2 and H-5.

36. The solid fuel air explosive composition of Claim 34, wherein said nano-sized metal  
10 particles have an average particle size of about 200 nm to about 500 nm.

37. An explosive having an annular design comprising:

a cylindrical shell of solid fuel air explosive, wherein said solid fuel air explosive is  
selected from the group consisting of reactive metal and metal composite; and  
15 a cylindrically shaped high explosive, wherein said cylindrical shell of solid fuel air  
explosive surrounds said cylindrically shaped high explosive.

38. The explosive of Claim 37, wherein said metal composite comprises:

about 60.0 to about 80.0 weight % of at least one reactive metal;  
20 about 4.0 to about 8.0 weight % of at least one binder; and

about 0.0 to about 36.0 weight % of an oxidizer.

39. The explosive of Claim 38, wherein said reactive metal is selected from the group consisting of nano-sized metal particles, metastable mechanical alloy and any combination thereof.

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40. The explosive of Claim 38, wherein said reactive metal is selected from the group consisting of nano-sized aluminum, nano-sized boron and nano-sized titanium, nano-sized magnesium, Al-Mg, Al-Mg-H, B-Mg, Al-B, Ti-B, Ti, B, Mg and H-2 and H-5.

10 41. The explosive of Claim 39, wherein said nano-sized metal particles have an average particle size of about 200 nm to about 500 nm.

42. The explosive of Claim 39, wherein said metastable mechanical metal alloy has an average particle size of about 1 $\mu$ m to about 50 $\mu$ m.

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43. The explosive of Claim 38, wherein said binder is selected from the group consisting of copolymer of vinylidene fluoride hexafluoropropylene, nitrocellulose, GAP and Zeon.

20 44. The explosive of Claim 38, wherein said oxidizer is selected from the group consisting of ammonium perchlorate, ammonium dinitramide and ammonium nitrate.

**45. The explosive of Claim 37, further comprising a plasticizer.**

**46. The explosive of Claim 37, further comprising a burn rate catalyst.**

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**THERMOBARIC EXPLOSIVE****ABSTRACT**

The invention disclosed herein relates to an explosive capable of enhanced combustion efficiently capable of sustaining a high pressure over a period of time in a confined environment, such as an air tight room or a cave, where oxygen may be in limited supply. An embodiment of the present invention is a metal composite that combines a binder, a reactive metal and an oxidizer. In another embodiment, a plasticizer and a catalyst may be added. In a preferred embodiment of the present invention, a solid fuel-air explosive (SFAE) having an annular design is used. In a typical annular design, a cylindrical shell of SFAE surrounds the cylindrically shaped high explosive. The SFAE may be selected from the group consisting of reactive metal and metal composite. In addition, the metal composite is formed from at least one reactive metal, at least one binder and an oxidizer.